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(54) Process and catalyst for producing reactor blend polyolefins.

(57) Polyolefin reactor blends obtained by polymerization of ethylene and higher alpha-olefins in the presence of a catalyst system comprising two or more metallocenes and alumoxane.

EP 0 128 046 A1

PROCESS AND CATALYST FOR PRODUCING REACTOR BLEND POLYOLEFINS

1 The present invention concerns catalyst and process for the
2 polymerization of ethylene and alpha-olefins. More
3 particularly, the invention relates to catalysts and process
4 for producing (co)polyolefin reactor blends of ethylene and
5 ethylene-alpha-olefin copolymers. The invention further
6 relates to a process for producing tailored (co)polyolefins
7 reactor blends through the proper selections of the catalysts
8 of this invention.

9 Reactor blends for purposes of this invention are mixtures
10 of two or more polymers of different physical properties
11 (density, melting point, comonomer content, etc.) produced
12 simultaneously in a single polymerization reactor. Catalyst
13 employed in the production of such polymer blends under steady
14 state conditions in one reactor will comprise two or more
15 distinct catalyst components, one predominately catalyzing the
16 formation of one polymer, the other predominately catalyzing
17 the formation of the other polymer.

18 DESCRIPTION OF THE PRIOR ART

19 It is known that certain metallocenes such as
20 bis(cyclopentadienyl) titanium and zirconium dialkyls in
21 combination with aluminum alkyl co-catalyst, form homogeneous
22 catalyst systems useful for the polymerization of ethylene.
23 German Patent Application 2,608,863 discloses the use of a
24 catalyst system for the polymerization of ethylene consisting of
25 bis(cyclopentadienyl) titanium dialkyl, aluminum trialkyl and
26 water. German Patent Application 2,608,933 discloses an
27 ethylene polymerization catalyst system consisting of (1)
28 zirconium metallocenes of the general formula
29 $(\text{cyclopentadienyl})_n \text{ZrY}_{4-n}$, wherein n stands for a number in
30 the range of 1 to 4, Y for R, CH_2AlR_2 , $\text{CH}_2\text{CH}_2\text{AlR}_2$ and
31 $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ wherein R stands for alkyl or metalloc alkyl,
32 (2) an aluminum trialkyl cocatalyst and (3) water.
33 European Patent Appln. No. 0035242 discloses a process for
34 preparing ethylene and atactic propylene polymers in the

1 presence of a halogen-free Ziegler catalyst system of (1)
2 cyclopentadienyl compound of the formula
3 $(\text{cyclopentadienyl})_n \text{MeY}_{4-n}$ in which n is an integer from 1
4 to 4, Me is a transition metal, especially zirconium, and Y is
5 either hydrogen, a C₁-C₅ alkyl or metalloc alkyl group or a
6 compound having the following general formula: CH₂AlR₂,
7 CH₂CH₂AlR₂ and CH₂CH(AlR₂)₂ in which R represents a
8 C₁-C₅ alkyl or metalloc alkyl group, and (2) an alumoxane.

9 The above disclosures demonstrate the usefulness of certain
10 metallocenes in combination with certain aluminum compounds for
11 the polymerization of ethylene and particularly polymerization
12 at a high activity rates. The references neither disclose
13 polyethylene/copolyethylene-alpha-
14 olefin reactor blends nor methods of producing such reactor
15 blends.

16 In "Molecular Weight Distribution And Stereoregularity Of
17 Polypropylenes Obtained With Ti(OC₄H₉)₄/Al(C₂H₅)₃
18 Catalyst System"; Polymer, Pg. 469-471, 1981, Vol. 22, April,
19 Doi, et al disclose propylene polymerization with a catalyst
20 which at about 41°C obtains a soluble catalyst and insoluble
21 catalyst fraction, one with "homogeneous catalytic centres" and
22 the other with "heterogeneous catalytic centres". The
23 polymerization at that temperature obtains polypropylene having
24 a bimodal molecular weight distribution.

25 It is also known to produce polymer blends by polymerizing
26 two or more polymerizable materials in two or more reactors
27 arranged in series. In accordance with such methods, a
28 polymerizate is produced in a first reactor which first
29 polymerizate is passed to a second reactor wherein a second
30 polymerizate is produced thereby obtaining a blend of the first
31 and second polymerizates.

32 It is highly desirable to be able to readily and simply
33 produce blends in a single reactor during which polyethylene
34 and copolyethylene-alpha-olefins are produced simultaneously.
35 Not only is a significant reduction in energy costs obtained,
36 but one obtains a uniform blending of the polymers and one can
37 simply "tailor" the polymers with respect to molecular weights,

1 weight fraction and the like to obtain blends evidencing
2 outstanding properties.

3 In view of the foregoing problems, it would be highly
4 desirable to provide a polymerization catalyst system of
5 sufficient activity to produce high quality blends of
6 ethylene-alpha olefin polymers. It is furthermore highly
7 desirable to be able to produce the blends of ethylene-alpha
8 olefin polymers directly in a single reactor.

9

10 The present invention provides a process for producing
11 (co)polyolefin reactor blends comprising polyethylene and
12 copolyethylene-alpha-olefins. The reactor blends are obtained
13 directly during a single polymerization process, i.e., the
14 blends of this invention are obtained in a single reactor by
15 simultaneously polymerizing ethylene and copolymerizing
16 ethylene with an alpha-olefin thereby eliminating expensive
17 blending operations. The invention furthermore provides a
18 catalyst system for the polymerization of ethylene and ethylene
19 copolymers simultaneously to provide polyethylene blends. The
20 process of producing reactor blends in accordance with this
21 invention can be employed in conjunction with other prior art
22 blending techniques, for example the reactor blends produced in
23 a first reactor can be subjected to further blending in a
24 second stage by use of a series of reactors.

25 Accordingly, there is provided a catalyst system for the
26 polymerization of reactor blends of polyethylene with
27 ethylene-alpha-olefin copolymers; said catalyst system
28 comprising (a) at least two different metallocenes and (b) an
29 alumoxane. The metallocenes employed in this invention are
30 organometallic coordination compounds which are
31 cyclopentadienyl derivatives of a transition metal of Groups
32 4b, 5b and 6b and include mono, di and tricyclopentadienyls and
33 their derivatives of the transition metal. The metallocenes
34 can be represented by the general formula

1 $(C_5R')_pR''_s(C_5R')_mMeQ_{3-p}$ or $R''_s(C_5R')_mMeQ'$,
2 wherein (C_5R') is a cyclopentadienyl or substituted
3 cyclopentadienyl, each R', which can be the same or different,
4 is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl,
5 aryl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon
6 atoms or two R' substituents together form a fused
7 C_4-C_6 ring, R'' is a C_1-C_4 alkylene radical, a dialkyl
8 germanium or silicone, or an alkyl phosphine or amine radical
9 bridging two (C_5R') rings, Q is a hydrocarbon radical such
10 as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having
11 from 1 to 20 carbon atoms or halogen and each Q can be the same or
12 different, Q' is an alkylidene radical having from 1 to about
13 20 carbon atoms, Me is a transition metal of Group 4b, 5b, 6b
14 of the Periodic Table (Chemical Rubber Company's Handbook of
15 Chemistry & Physics, 48th Edition), s is 0 or 1, p is 0, 1 or
16 2; when p = 0, s = 0; m is 4 when s is 1 and m is 5 when s is 0.

17 The ratios of one metallocene to the second metallocene
18 will be a function of both the chemical composition of the
19 metallocenes as well as the blend being tailored; accordingly,
20 the ratio of the two metallocenes can vary greatly and, hence,
21 is limited only for the purpose of producing the blends.

22 The present invention also provides a process for producing
23 polyolefin reactor blends. The process comprises polymerizing
24 ethylene and higher alpha-olefins in the presence of the
25 catalyst system described above.

26 DETAILED DESCRIPTION OF THE INVENTION

27 The present invention is directed towards a catalytic
28 process for the polymerization of ethylene and one or more
29 alpha-olefins to polyethylene-copolyethylene-alpha-olefin
30 reactor blends. The polymers are intended for fabrication into
31 articles by extrusion, injection molding, thermoforming,
32 rotational molding, and the like. In particular, the polymer
33 blends of this invention are blends of polyethylenes such as
34 high density polyethylene (HDPE) and linear low density
35 polyethylene (LLDPE) and with copolyethylene higher
36 alpha-olefins having from 3 to about 10 carbon atoms and

1 preferably 4 to 8 carbon atoms. Illustrative of the higher
2 alpha-olefins are propylene, butene-1, hexene-1 and octene-1.
3 Preferably, the alpha-olefin is propylene or butene-1.

4 In the process of the present invention, ethylene, together
5 with the alpha-olefins, is polymerized in the presence of a
6 homogeneous catalyst system comprising at least two different
7 metallocenes and an alumoxane.

8 The alumoxanes are well known in the art and are polymeric
9 aluminum compounds which can be represented by the general
10 formulae $(R-Al-O)_n$, which is a cyclic compound and
11 $R(R-Al-O)_n AlR_2$, which is a linear compound. In the
12 general formula R is a C₁-C₅ alkyl group such as, for
13 example, methyl, ethyl, propyl, butyl and pentyl and n is an
14 integer from 1 to about 20 and preferably from about 1 to about
15 4. Most preferably, R is methyl and n is 4. Generally, in the
16 preparation of alumoxanes from, for example, aluminum trimethyl
17 and water, a mixture of the linear and cyclic compounds are
18 obtained.

19 The alumoxane can be prepared in various ways. Preferably,
20 they are prepared by contacting water with solution of aluminum
21 trialkyl, such as, for example, aluminum trimethyl, in a
22 suitable organic solvent such as benzene or an aliphatic
23 hydrocarbon. For example, the aluminum alkyl is treated with
24 water in form of a moist solvent or the aluminum alkyl such as
25 aluminum trimethyl can be desirably contacted with a hydrated
26 salt such as hydrated copper sulfate.

27 Preferably, the alumoxane is prepared in the presence of a
28 hydrated copper sulfate. The method comprises treating a
29 dilute solution of aluminum trimethyl in, for example, toluene,
30 with copper sulfate represented by the general formula
31 CuSO₄.5H₂O. The ratio of copper sulfate to aluminum
32 trimethyl is desirably about 1 mole of copper sulfate for 5
33 moles of aluminum trimethyl. The reaction is evidenced by the
34 evolution of methane.

35 The dual metallocene system usefully employed in accordance
36 with this invention are the mono, di and tricyclopentadienyl or
37 substituted cyclopentadienyl metallocenes and preferably the

1 titanium (IV) and zirconium (IV) metallocenes. The
2 metallocenes are represented by the general formula
3 $(C_5R'^m)_p R''_s (C_5R'^m)_q MeQ_{3-p}$ and
4 $R''_s (C_5R'^m)_2 MeQ'$ wherein $(C_5R'^m)$ is cyclopentadienyl
5 or substituted cyclopentadienyl, each R' is the same or
6 different and is hydrogen or a hydrocarbyl radical such as
7 alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radicals
8 containing from 1 to 20 carbon atoms or two carbon atoms are
9 joined together to form a C_4-C_6 ring, R'' is a C_1-C_4
10 alkylene radical, a dialkyl germanium or silicone, or an alkyl
11 phosphine or amine radical bridging two $(C_5R'^m)$ rings, Q is
12 a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl,
13 or arylalkyl radical having from 1-20 carbon atoms or halogen
14 and can be the same or different, Q' is an alkylidene radical
15 having from 1 to about 20 carbon atoms, s is 0 or 1, p is 0, 1
16 or 2; when p is 0, s is 0, m is 4 when s is 1 and m is 5 when s
17 is 0 and Me is a Group 4b, 5b or 6b transition metal and most
18 preferably zirconium or titanium.

19 Exemplary hydrocarbyl radicals are methyl, ethyl, propyl,
20 butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl,
21 decyl, cetyl, 2-ethylhexyl, phenyl, and the like.

22 Exemplary alkylene radicals are methylene, ethylene,
23 propylene, and the like.

24 Preferred examples of substituent Q are methyl,
25 phenyl or chloride.

26 Exemplary halogen atoms include chlorine, bromine
27 and iodine and of these halogen atoms, chlorine is
28 preferred.

29 Exemplary of the alkylidene radicals are methyldene,
30 ethyldene and propyldene.

31 Preferably the catalyst comprises at least two
32 zirconocenes or at least one titanocene and at least one
33 zirconocene.

34 Illustrative but non-limiting examples of the titanocenes
35 which can be usefully employed in accordance with
36 this invention are bis(cyclopentadienyl) titanium

1 diphenyl, the carbene represented by the formula
2 $Cp_2Ti=CH_2 \cdot Al(CH_3)_2Cl$, and derivatives of this
3 reagent such as $Cp_2Ti=CH_2 \cdot Al(CH_3)_3$,
4 $(Cp_2TiCH_2)_2$, $Cp_2TiCH_2CH(CH_3)CH_2$,
5 $Cp_2Ti=CHCH_2CH_2$, $Cp_2Ti=CH_2 \cdot AlR'''_2Cl$, wherein Cp
6 is a cyclopentadienyl or substituted cyclopentadienyl
7 radical,

1 and R''' is an alkyl, aryl or alkylaryl radical having from
2 1-18 carbon atoms; substituted bis(Cp)Ti(IV) compounds such as
3 bis(indenyl)Ti diphenyl or dichloride,
4 bis(methylcyclopentadienyl)Ti diphenyl or dihalides and other
5 dihalide complexes; dialkyl, trialkyl, tetra-alkyl and
6 penta-alkyl cyclopentadienyl titanium compounds such as
7 bis(1,2-dimethylcyclopentadienyl)Ti diphenyl or dichloride,
8 bis(fluorenyl)Ti dichloride, bis(1,2-diethylcyclopentadienyl)Ti
9 diphenyl or dichloride and other dihalide complexes; silicone,
10 phosphine, amine or carbon bridged cyclopentadiene complexes,
11 such as dimethyl silyldicyclopentadienyl titanium diphenyl or
12 dichloride, methyl phosphine dicyclopentadienyl titanium
13 diphenyl or dichloride, methylenedicyclopentadienyl titanium
14 diphenyl or dichloride and other dihalide complexes.

15 Illustrative but non-limiting examples of the zirconocenes
16 which can be usefully employed in accordance with this
17 invention are bis(cyclopentadienyl)zirconium diphenyl,
18 bis(cyclopentadienyl)zirconium dimethyl; the alkyl substituted
19 cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium
20 dimethyl, bis(β -phenylpropylcyclopentadienyl)zirconium
21 dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl and
22 dihalide complexes of the above; di-alkyl, tri-alkyl,
23 tetra-alkyl, and penta-alkyl cyclopentadienes, such as
24 bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis
25 (1,2-dimethylcyclopentadienyl)zirconium dimethyl,
26 bis(1,3-diethylcyclopentadienyl)zirconium dimethyl and dihalide
27 complexes of the above; silicone, phosphorus, and carbon
28 bridged cyclopentadiene complexes such as
29 dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide,
30 methylphosphine dicyclopentadienyl zirconium dimethyl or
31 dihalide, and methylene dicyclopentadienyl zirconium dimethyl
32 or dihalide, carbenes represented by the formulae
33 Cp₂Zr=CH₂P(C₆H₅)₂CH₃, and derivatives of these
34 compounds such as Cp₂ZrCH₂CH(CH₃)CH₂.

35 The ratio of aluminum in the alumoxane to total metal in
36 the metallocenes can be in the range of 0.5:1 to
37 10⁵:1, and preferably 5:1 to 1000:1. The molar

1 ratio of the metallocenes can vary over a wide range and in
2 accordance with this invention the molar ratios are controlled
3 by the product polymer blend desired.

4 The reactivity ratios of the metallocenes in general are
5 obtained by methods well known such as, for example, as
6 described in "Linear Method for Determining Monomer Reactivity
7 Ratios in Copolymerization", M. Fineman and S. D. Ross, J.
8 Polymer Science 5, 259 (1950) or "Copolymerization", F. R. Mayo
9 and C. Walling, Chem. Rev. 46, 191 (1950) incorporated herein
10 in its entirety by reference. For example, to determine
11 reactivity ratios the most widely used copolymerization model
12 is based on the following equations:

$$\begin{array}{l} 13 \quad M_1^* + M_1 \frac{k_{11}}{k_{12}} M_1^* \quad (1) \\ 14 \quad M_1^* + M_2 \frac{k_{12}}{k_{21}} M_2^* \quad (2) \\ 15 \quad M_2^* + M_1 \frac{k_{21}}{k_{22}} M_1^* \quad (3) \\ 16 \quad M_2^* + M_2 \frac{k_{22}}{k_{11}} M_2^* \quad (4) \end{array}$$

17 where M_i refers to a monomer molecule which is arbitrarily
18 designated i (where $i = 1, 2$) and M_i^* refers to a growing
19 polymer chain to which monomer i has most recently attached.

20 The k_{ij} values are the rate constants for the indicated
21 reactions. Thus, k_{11} represents the rate at which an
22 ethylene unit inserts into a growing polymer chain in which the
23 previously inserted monomer unit was also ethylene. The
24 reactivity rates follow as: $r_1 = k_{11}/k_{12}$ and $r_2 =$
25 k_{22}/k_{21} wherein k_{11} , k_{12} , k_{22} and k_{21} are the rate
26 constants for ethylene (1) or propylene (2) addition to a
27 catalyst site where the last polymerized monomer is an
28 ethylene (k_{1X}) or propylene (k_{2X}).

29 In Table I the ethylene-propylene reactivity rates r_1 and
30 r_2 are listed for several metallocenes. It can be seen that
31 with increased steric interaction at the monomer coordination
32 site r_1 increases, i.e. the tendency for ethylene
33 polymerization increases over propylene polymerization.

1 It can be seen from Table I that if one desires a blend
 2 comprising HDPE/ethylene-propylene copolymer one would select
 3 bis(pentamethylcyclopentadienyl)ZrCl₂ and
 4 bis(cyclopentadienyl)Ti diphenyl or
 5 dimethylsilyldicyclopentadienyl zirconium dichloride in ratios
 6 of 5:1 to 1:1 whereas if one desires a blend
 7 comprising LLDPE/ethylene-propylene one would select
 8 bis(cyclopentadienyl)Zr dimethyl or
 9 bis(methylcyclopentadienyl)ZrCl₂ and bis(cyclopentadienyl)Ti
 10 diphenyl or dimethylsilyldicyclopentadienyl ZrCl₂ in ratios
 11 of 10:1 to 1:1.

12 Desirably, the metallocene molar ratio will be 100:1
 13 to 1:100, and preferably 10:1 to 1:10. The
 14 specific metallocenes selected and their molar ratios are
 15 depended upon the molecular composition desired for the
 16 component polymers and the overall composition desired for the
 17 blend. In general, the component catalyst used in a reactor
 18 blend catalyst mixture will each have r values which are
 19 different in order to produce final polymer compositions which
 20 comprise blends of two or more polymers.

TABLE I

22	Catalyst	r ₁	r ₂
23	Cp ₂ Ti=CH ₂ · Al(Me) ₂ Cl	24	0.0085
24	Cp ₂ TiPh ₂	19.5±1.5	0.015±.002
25	Me ₂ SiCp ₂ ZrCl ₂	24±2	0.029±.007
26	Cp ₂ ZrCl ₂	48±2	0.015±.003
27	(MeCp) ₂ ZrCl ₂	60	
28	(Me ₅ Cp) ₂ ZrCl ₂	250±30	.002±0.001
29	[Cp ₂ ZrCl] ₂ O	50	0.007

30 The solvents used in the preparation of the catalyst system
 31 are inert hydrocarbons, in particular a hydrocarbon that is
 32 inert with respect to the catalyst system. Such solvents are
 33 well known and include, for example, isobutane, butane,
 34 pentane, hexane, heptane, octane, cyclohexane,
 35 methylcyclohexane, toluene, xylene and the like.

1 The catalyst systems described herein are suitable for
2 producing polymer product blends in solution, slurry or a gas
3 phase polymerizations and over a wide range of temperatures and
4 pressures. For example, such temperatures may be in the range
5 of -60 to 280°C and especially in the range of
6 50 to 160 °C. The pressures employed in the
7 process of the present invention are those well known for
8 example, in the range of 1 to 500 atmospheres and
9 greater.

10 In a solution phase polymerization the alumoxane and
11 metallocene can be employed as a homogeneous catalyst system.
12 The alumoxane is preferably dissolved in a suitable solvent,
13 typically in inert hydrocarbon solvent such as toluene, xylene,
14 and the like in molar concentrations of 0.1 to 3.0,
15 however greater or lesser amounts can be employed.

16 The soluble metallocenes can be converted to supported
17 heterogeneous catalyst by depositing said metallocenes on
18 typical catalyst supports such as, for example, silica,
19 alumina, and polyethylene. The solid catalysts in combination
20 with an alumoxane can be usefully employed in slurry and gas
21 phase olefin polymerizations.

22 After polymerization and deactivation of the catalyst, the
23 product polymer blend can be recovered by processes well known
24 in the art for removal of deactivated catalysts and solution.
25 The solvents may be flashed off from the polymer solution and
26 the polymer obtained extruded into water and cut into pellets
27 or other suitable comminuted shapes.

28 Pigments, antioxidants and other additives, as is known in
29 the art, may be added to the polymer.

30 The polymer product obtained in accordance with this
31 invention will have a weight average molecular weight in the
32 range of 500 to 2,000,000 and preferably 10,000 to
33 500,000. The component polymers in the reactor blend can
34 have the same or different average molecular weights and
35 comonomer composition; however, it is preferable for most end
36 uses that the average molecular weights and comonomer
37 composition be different.

1 Illustrative, but nonlimiting examples of reactor blends
2 which can be produced in accordance with this invention are
3 HDPE/EPR copolymer, LLDPE/EPR copolymer, HDPE/LLDPE and
4 HDPE/LLDPE/EPR copolymer blends. These polymers demonstrate
5 superior properties such as for example impact resistance and
6 tear strength and process more easily than the individual
7 component polymers.

8 The polymers produced by the process of this present
9 invention are capable of being fabricated into a wide variety
10 of articles, as is known for blend of ethylene and copolymers
11 of ethylene and higher alpha-olefins. The present invention is
12 illustrated by the following examples.

13 EXAMPLES

14 In the examples following the molecular weights were
15 determined on a Water's Associates Model No. 150C GPC. The
16 measurements were made by dissolving polymer samples in hot
17 trichlorobenzene (TCB) and filtered. The GPC (Gel Permeation
18 Chromotography) runs were performed at 145°C in TCB at 1.5
19 ml/min using two Shodex A80M/S columns of 9.4 mm internal
20 diameter from Perkins Elmer Inc. 300 milliliter of 3.1 percent
21 solutions in TCB were injected and the chromatographic runs
22 monitored at sensitivity equal -64 and scale factor equal 65.
23 The samples were run in duplicate. The integration parameters
24 were obtained with a Water's Associates data module. An
25 antioxidant, N-phenyl-2-naphthylamine, was added to all samples.

26 In the examples following the alumoxane was prepared in the
27 following manner:

28 600cc of a 14.5% solution of trimethylaluminum (TMA) in
29 heptane was added in 30cc increments at 5 minute intervals,
30 with rapid stirring, to 200cc toluene in a Zipperclave reactor
31 under nitrogen and maintained at 100°C. Each increment was
32 immediately followed by the addition of 0.3cc water. The
33 reactor was vented of methane after each addition. Upon
34 completion of the addition, the reactor was stirred for 6 hours
35 while maintaining the temperature at 100°C. The mixture,

1 containing soluble alumoxane is allowed to cool to room
2 temperature and settle. The clear solution containing the
3 soluble alumoxane is separated by decantation from the solids.

4

5 Example 1(a) - Reactor blend

6 A 1-liter stainless steel pressure vessel, equipped with an
7 incline blade stirrer, an external water jacket for temperature
8 control, a septum inlet and vent line, and a regulated supply
9 of dry ethylene, propylene and nitrogen, was dried and
10 deoxygenated with a nitrogen flow. 400cc of dry, degassed
11 toluene was introduced directly into the pressure vessel. 25cc
12 of 0.64 molar (in total aluminum) alumoxane was injected into
13 the vessel by a gas tight syringe through the septum inlet and
14 the mixture was stirred at 1,200 rpm's and 50°C for 5 minutes
15 at zero (0) psig of nitrogen. 1.12 mg bis(cyclopentadienyl)
16 titanium phenyl dissolved in 2.0 ml of dry, distilled toluene
17 was injected through the septum inlet into the vessel.
18 Similarly, 0.107 mg. bis(pentamethylcyclopentadienyl) zirconium
19 dimethyl in 2.0 ml dry, distilled toluene was injected. The
20 solution was saturated with 200cc propylene at a pressure of
21 165 psig. Thereafter ethylene at 25 psig was passed into the
22 vessel for 60 minutes while maintaining the temperature at
23 50°C at which time the reaction was stopped by rapidly
24 venting and cooling. The copolymer was evaporated to dryness,
25 weighed and analyzed by GPC and IR. 62 gms of a blend of
26 polyethylene and EPR copolymer which analyzed for 6 mole %
27 propylene and having a Mn of 16,500 and a Mw of 41,800 was
28 recovered.

29 Example 1(b) - Use of One Metallocene -

30 bis(pentamethylcyclopentadienyl)Zirconiumdimethyl

31 A 1-liter stainless steel pressure vessel, equipped with an
32 incline blade stirrer, an external water jacket for temperature
33 control, a septum inlet and vent line, and a regulated supply
34 of dry ethylene, propylene and nitrogen, was dried and
35 deoxygenated with a nitrogen flow. 400cc of dry, degassed

1 toluene was introduced directly into the pressure vessel. 25cc
2 of 0.64 molar (in total aluminum) alumoxane was injected into
3 the vessel by a gas tight syringe through the septum inlet and
4 the mixture was stirred at 1,200 rpm's and 50°C for 5 minutes
5 at zero (0) psig of nitrogen. 0.122 mg
6 bis(pentamethylcyclopentadienyl)zirconium dimethyl dissolved in
7 2.0 ml of dry, distilled toluene was injected through the
8 septum inlet into the vessel. Liquid propylene (200cc) was
9 added from a calibrated addition vessel resulting in a
10 propylene pressure of 153 psig. Thereafter ethylene at 25 psig
11 was passed into the vessel for 90 minutes while maintaining the
12 temperature at 50°C at which time the reaction was stopped by
13 rapidly venting and cooling. 76 gms of polyethylene which
14 analyzed for 3.4% propylene and having a \bar{M}_n of 15,300 and a \bar{M}_w
15 of 36,400 was recovered. The analysis was performed as in
16 Example 1(a).

17 Example 1(c) - Use of One Metallocene -
18 bis(cyclopentadienyl)Tidiphenyl

19 A 1-liter stainless steel pressure vessel, equipped with an
20 incline blade stirrer, an external water jacket for temperature
21 control, a septum inlet and vent line, and a regulated supply
22 of dry ethylene, propylene and nitrogen, was dried and
23 deoxygenated with a nitrogen flow. 400cc of dry, degassed
24 toluene was introduced directly into the pressure vessel. 25cc
25 of 0.64 molar (in total aluminum) alumoxane was injected into
26 the vessel by a gas tight syringe through the septum inlet and
27 the mixture was stirred at 1,200 rpm's and 50°C for 5 minutes
28 at zero (0) psig of nitrogen. 1.04 mg bis(cyclopentadienyl)
29 titanium phenyl dissolved in 2.0 ml of dry, distilled toluene
30 was injected through the septum inlet into the vessel. Liquid
31 propylene (200cc) was added from a calibrated addition vessel
32 resulting in a propylene pressure of 165 psig. Thereafter
33 ethylene at 25 psig was passed into the vessel for 90 minutes
34 while maintaining the temperature at 50°C at which time the
35 reaction was stopped by rapidly venting and cooling. 14.4 gms
36 of polyolefin which analyzed for 65% ethylene and 35% propylene

1 and having a \bar{M}_n of 45,400 and a \bar{M}_w of 137,000 was recovered.
2 The analysis was performed as in Example 1(a).

3 Example 2 - Use of Two Different Metallocenes

4 A 1-liter stainless steel pressure vessel, equipped with an
5 incline blade stirrer, an external water jacket for temperature
6 control, a septum inlet and vent line, and a regulated supply
7 of dry ethylene, propylene and nitrogen, was dried and
8 deoxygenated with a nitrogen flow. 400cc of dry, degassed
9 toluene was introduced directly into the pressure vessel.
10 10.0cc of 0.83 molar (in total aluminum) alumoxane was injected
11 into the vessel by a gas tight syringe through the septum inlet
12 and the mixture was stirred at 1,200 rpm's and 80°C for 5
13 minutes at zero (0) psig of nitrogen. 2.127 mg
14 bis(pentamethylcyclopentadienyl) zirconium dichloride dissolved
15 in 2.0 ml of dry, distilled toluene was injected through the
16 septum inlet into the vessel. Similarly, 0.2628 mg
17 bis(methylcyclopentadienyl) zirconium dichloride in 0.25 ml
18 dry, distilled toluene was injected. The solution was
19 saturated with propylene at a pressure of 111 psig for 15
20 seconds. Thereafter ethylene at 15 psig was passed into the
21 vessel for 20 minutes while maintaining the temperature at
22 80°C and the pressure at 126° psig at which time the
23 reaction was stopped by rapidly venting and cooling. 18.0 gms
24 of a blend of PE and EPR copolymer analyzed for 7.1 mole %
25 propylene and having a \bar{M}_n of 2,000 and a \bar{M}_w of 8,300 was
26 recovered. A fractionation analysis was performed by stirring
27 a 10 g portion of this solid product for one hour in 100 ml of
28 toluene. The slurry was filtered and washed with 10 ml of
29 fresh toluene. The copolymer in solution and the solid product
30 were separately evaporated to dryness, weighed and analyzed by
31 GPC and IR.

32 The soluble product (7.0g) had a \bar{M}_n of 2,200 and a \bar{M}_w of
33 11,900 and analyzed for 30 mole % propylene. The insoluble
34 fraction had an \bar{M}_n of 3000 and a \bar{M}_w of 7,400 and analyzed to
35 contain 4.8% propylene.

Example 3

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene, propylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400cc of dry, degassed toluene was introduced directly into the pressure vessel. 10cc of alumoxane molar (8.3 m moles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpm's and 50°C for 5 minutes at zero (0) psig of nitrogen. 0.539 mg bis(methylcyclopentadienyl) zirconium dimethyl dissolved in 2.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel. Similarly, 1.03 mg bis(pentamethylcyclopentadienyl) zirconium dichloride in 2.0 ml dry, distilled toluene was injected. The solution was saturated with 200cc propylene at a pressure of 111 psig for 15 seconds. Thereafter ethylene at 25 psig (C_3/C_2 liquid ratio = 16) was passed into the vessel for 20 minutes while maintaining the temperature at 50°C at which time the reaction was stopped by rapidly venting and cooling. 30.0 gms of a blend of LLDPE and EP copolymer analyzed for 3.6% propylene and having a \bar{M}_n of 5,600 and a \bar{M}_w of 17,300 was recovered. The fractionation analysis, GPC & IR performed as in Example 2 yielded 3.0 gms of a soluble fraction having a \bar{M}_n of 3,500, a \bar{M}_w of 16,000 and mole % of C_3^{∞} of 20.6. The insoluble fraction (7.0 gms) had a \bar{M}_n of 5,400, a \bar{M}_w of 16,400 and mole % C_3^{∞} of 2.9%.

CLAIMS:

1. A catalyst system for the production of reactor blend polymers, said catalyst comprising (a) at least two different organometallic coordination compounds which are derivatives of mono, di or tricyclopentadienyls with Group 4b, 5b and 6b transition metal, the compounds having different reactivity with respect to the monomers employed and (b) an alumoxane.

2. A homogeneous catalyst system for the production of reactor blend polymers comprising a blend of polyethylene and an ethylene-olefin copolymer; said catalyst comprising:

(a) at least two metallocenes having represented by the general formula

$(C_5R')_pR''_s(C_5R'_m)_sMeQ_{3-p}$ or
 $R''_s(C_5R'_m)_2MeQ'$ each having different reactivity ratios, and

(b) an alumoxane

wherein $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' which can be the same or different is hydrogen or a hydrocarbyl radical or two substituents together form a fused C_4-C_6 ring, R'' is a C_1-C_4 alkylene radical, a dialkyl germanium or silicone, or an alkyl phosphine or amine radical bridging two $(C_5R'_m)$ rings, Q is a hydrocarbon radical or halogen and can be the same or different, Q' is an alkylidene radical having from 1 to 20 carbon atoms, Me is a transition metal of Group 4b, 5b and 6b, s is 0 or 1, p is 0, 1 or 2; when p = 0, s = 0; m is 4 when s is 1; m is 5 when s is 0.

3. The catalyst system of claim 2 wherein Q is methyl, phenyl or chloride.

4. The catalyst system of claim 2 or claim 3, wherein Me is selected from zirconium and titanium.

5. The catalyst system of claim 4 comprising at least 2 zirconocenes.

6. The catalyst system of claim 4 comprising at least 1 titanocene and 1 zirconocene.

7. The catalyst system of claim 5 comprising bis (methylcyclopentadienyl) zirconium dichloride and bis (penta-methylcyclopentadienyl) zirconium dichloride.

8. A process for producing a reactor blend comprising polymerizing ethylene and at least alpha-olefin simultaneously in the presence of the catalyst system of any of claims 1 to 7.

9. The process of claim 8 wherein the polymer blend comprises a blend of polyethylene and copolyethylene-propylene.

10. The process of claim 9 wherein the polyethylene is LLDPE or HDPE.



European Patent
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EUROPEAN SEARCH REPORT

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Application number

EP 84 30 3806

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. *)	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim		
A	EP-A-0 069 951 (HOECHST) * Claims 1-8 *	1	C 08 F 10/00 C 08 F 4/62	
A,D	EP-A-0 035 242 (HANSJÖRG SINN) * Claims 1,2 *	1		
A	GB-A- 978 893 (HOECHST) * Claims 1,5,7; page 2, lines 26-33 *	1		
-----			TECHNICAL FIELDS SEARCHED (Int. Cl. *)	

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The present search report has been drawn up for all claims				
Place of search THE HAGUE	Date of completion of the search 13-09-1984	Examiner WEBER H.		
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		